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(54) Title: METHOD FOR PREDICTING A PHYSICAL PROPERTY OF A RESIDUAL HYDROCARBONACEOUS MATERIAL (57) Abstract <p>The present invention provides a method for predicting a physical property of a residual hydrocarbonaceous material comprising the steps of: a) selecting a set of residual hydrocarbonaceous materials of different quality; b) determining a physical property of the residual hydrocarbonaceous materials by conventional measurement; c) measuring the (near) infrared spectra of the residual hydrocarbonaceous materials; d) selecting in the spectral region a range of wavelengths, and using the absorbance values measured at these wavelengths as an input for multivariate statistical analysis or a neural network; d) correlating the absorbance values obtained with the physical property as determined under b) by means of multivariate statistical analysis or a neural network and generating a predictive model; and subsequently e) applying this predictive model to (near) infrared spectra, taken under the same conditions, for residual hydrocarbonaceous materials of an unknown physical property, thus providing the physical property of the unknown residual hydrocarbonaceous material.</p>		

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METHOD FOR PREDICTING A PHYSICAL PROPERTY
OF A RESIDUAL HYDROCARBONACEOUS MATERIAL

The present invention relates to a method for predicting a physical property of a residual hydrocarbonaceous material by correlation of its (near) infrared spectrum to the physical property.

5 The use of (near) infrared spectroscopy to control processes for the preparation of petroleum products is known for instance from "Hydrocarbon Processing", February 1995, pages 86-92. The processes described in said document include the preparation of gasolines and
10 gas oils by the controlled blending of various components. The quality of the final product is determined on-line using a Fourier transform-type of spectrometer which is connected to a computer. In this way the use of blend tables can advantageously be
15 avoided.

Another type of process widely applied in petroleum industry, in respect of which it would be highly advantageous to control continuously the product quality by means of (near) infrared spectroscopy, is
20 the preparation of bitumen compositions by blending various streams of different grades of bitumen. Attempts to use (near) infrared spectroscopy for controlling the quality of bitumen compositions have, however, been rather disappointing so far, which can
25 most likely be attributed to the very heavy components of which bituminous materials are built up.

In this respect reference is made to "Rapid Prediction and Evaluation of Bitumen Properties by Near Infrared Spectroscopy", G. Svehinsky and I. Ishia,
30 which paper was presented at the Third Annual Meeting of RILEM Committee TC PBM-152, Madrid, Spain, June

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1995. In said paper the use has been described, without any details, of the reflection of near infrared radiation for characterization and prediction of different bitumen parameters.

5 Object of the present invention is to provide an advanced method for predicting a physical property of residual hydrocarbonaceous materials such as crude oil residues including residues, residual fuel oils and bituminous materials using (near) infrared spectra.

10 The present invention therefore provides a method for predicting a physical property of a residual hydrocarbonaceous material comprising the steps of:

- a) selecting a set of residual hydrocarbonaceous materials of different quality;
- 15 b) determining a physical property of the residual hydrocarbonaceous materials by conventional measurement;
- c) measuring the (near) infrared spectra of the residual hydrocarbonaceous materials;
- 20 d) selecting in the spectral region a range of wavelengths, and using the absorbance values measured at these wavelengths as an input for multivariate statistical analysis or a neural network;
- 25 e) correlating the absorbance values obtained with the physical property as determined under b) by means of multivariate statistical analysis or a neural network and generating a predictive model; and subsequently
- 30 f) applying this predictive model to (near) infrared spectra, taken under the same conditions, for residual hydrocarbonaceous materials of an unknown physical property, thus providing the physical property of the unknown residual hydrocarbonaceous material.

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By means of the above method it is for instance

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possible to control continuously the quality of a hydrocarbonaceous feedstock and/or the product derived therefrom.

According to the present invention the (near)
5 infrared spectra of a relatively large set of residual hydrocarbonaceous materials (suitably at least 10, preferably at least 50) of different quality are measured.

The number of hydrocarbonaceous materials of
10 different quality in the set is important since this determines the generality and applicability of any subsequent statistical predictive pool.

The light from the (near) infrared region has wavelengths in the range of from 1000 to 10,000 nm,
15 preferably in the range of from 1500 to 3000 nm, more preferably in the range of from 1640 to 2630 nm or one or more selected intervals thereof.

The spectra obtained can be analysed, together with determinations of the physical property by conventional
20 measurements, using multivariate statistical analysis techniques such as Partial Least Squares, Multiple Linear Regression, Reduced Rank Regression, Principal Component Analysis and the like, or neural networks.

The above-mentioned multivariate statistical
25 techniques and neural networks are as such known to those skilled in the art and will therefore not be described in detail.

Suitably, the absorbance values are measured at a large number of the wavelengths in the spectral region.
30 Suitably, the absorbance values are measured at the whole range of wavelengths in the spectral region or at one or more selected intervals thereof.

Subsequently a predictive model is generated that can be applied to the (near) infrared spectra, taken
35 under the same conditions, for residual hydrocarbonaceous materials of an unknown physical

property.

Correlation of the absorbance values with the physical property of the residual hydrocarbonaceous materials as determined under b) is done by known techniques mentioned before such as multiple linear regression or partial least squares regression.

The residual hydrocarbonaceous materials of which a physical property can be determined in accordance with the present invention comprise for instance heavy gas oils, crude oil residues, residual fuel oils and bituminous materials.

Crude oil residues may consist of straight run residues such as long (atmospheric) and short (vacuum) residues, processed residue streams such as thermally cracked, hydrocracked or catalytically cracked residues. Residual fuel oils may consist of residues and any known diluent streams such as any refinery stream to influence residue properties, and may contain any known additive such as stabilising or emulsifying agents.

Suitable bituminous materials include naturally occurring bitumens or derived from a mineral oil. Also blends of various bituminous materials can be analysed. Examples of suitable bituminous materials include distillation or "straight-run bitumens", cracked residues, polymer-modified bitumens, precipitation bitumens, e.g. propane bitumens, blown bitumens, e.g. catalytically blown bitumen, and mixtures thereof.

Other suitable bituminous materials include mixtures of one or more of these bitumens with extenders (fluxes) such as petroleum extracts, e.g. aromatic extracts, distillates or residues, or with oils. The bituminous materials to be analysed may contain any emulsifying agent known in the art.

The above-mentioned residual hydrocarbonaceous materials to be analysed by means of (near) infrared

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spectroscopy have suitably a temperature of at least 50°C, preferably a temperature of at least 100°C.

The physical properties to be determined include properties such as penetration (PEN), softening point, density, viscosity, flash point, storage and handling stability, compatibility, and chemical composition related properties such as aromaticity, C7 asphaltenes content, wax content, paraffin content, volatility and retained PEN (after RTFOT (Rolling thin film oven test)), microcarbon residue, Conradson carbon residue and feedstock assessment parameters.

In accordance with the present invention two or more physical properties, e.g. softening point and PEN, of a residual hydrocarbonaceous material can be determined simultaneously.

The present invention will now be illustrated by means of the following Example.

Example 1

A set of 72 bituminous materials of different quality was selected. The samples were all rated for penetration and softening point values using the ASTM D 5 and ASTM D 36 methods respectively. The samples were subsequently measured in the near infrared region having wavelengths in the range of from 1640 to 2630 nm. Samples of the bituminous materials were in turn contained in a transmission cell at a temperature of 200 °C and the near infrared spectra were recorded. A predictive model was generated using partial least squares regression as explained before. The standard deviations of prediction are 3 dmm for penetration in the range 20-140 dmm, and 0.7 °C for softening point in the range 42-62 °C, as determined by the leave-one-out cross-validation method.

Example 2

A set of 75 thermally cracked residues of different quality was selected. The samples were all rated for

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Micro Carbon Residue content and viscosity using the ASTM D-4530-93 and ASTM D-445-94 methods respectively. The samples were subsequently measured in the near infrared region having wavelengths in the range of from 5 1640 to 2630 nm. Samples of the residues were in turn contained in a transmission cell at a temperature of 200 °C and the near infrared spectra were recorded. A predictive model was generated using partial least squares regression as explained before. The standard 10 deviations of predictions are 0.4 %w/w for Micro Carbon Residue content in the range of 24.3 - 35.2 %w/w, and 6.5% for viscosity in the range of 65 - 554 cSt, as determined by the leave-one-out cross validation method.

15 It will be clear from the foregoing that the present invention provides a very attractive method for predicting physical properties of residual hydrocarbonaceous materials.

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C L A I M S

1. A method for predicting a physical property of a residual hydrocarbonaceous material comprising the steps of:
 - 5 a) selecting a set of residual hydrocarbonaceous materials of different quality;
 - b) determining a physical property of the residual hydrocarbonaceous materials by conventional measurement;
 - 10 c) measuring the (near) infrared spectra of the residual hydrocarbonaceous materials;
 - d) selecting in the spectral region a range of wavelengths, and using the absorbance values measured at these wavelengths as an input for multivariate statistical analysis or a neural
15 network;
 - e) correlating the absorbance values obtained with the physical property as determined under b) by means of multivariate statistical analysis or a neural network and generating a predictive model; and
20 subsequently
 - f) applying this predictive model to (near) infrared spectra, taken under the same conditions, for residual hydrocarbonaceous materials of an unknown physical property, thus providing the physical
25 property of the unknown residual hydrocarbonaceous material.
2. The method according to claim 1, wherein the (near) infrared region has wavelengths in the range of from 1000 to 10,000 nm.
- 30 3. The method according to claim 2, wherein the wavelengths range of from 1500 to 3000 nm.
4. The method according to any one of claims 1 to 3, wherein the set of residual hydrocarbonaceous materials is at least 50.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/35 G01N33/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 09362 A (SHELL CANADA LTD ;SHELL INT RESEARCH (NL)) 28 April 1994 see claim 1 ---	1
A	WO 94 08226 A (SHELL CANADA LTD ;SHELL INT RESEARCH (NL)) 14 April 1994 see claim 1 ---	1
A	EP 0 304 232 A (BP OIL INT) 22 February 1989 see claims 1,12 ---	1
A	EP 0 285 251 A (BP OIL INT ;BP CHEM INT LTD (GB)) 5 October 1988 see claim 1 -----	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/04599

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO-A-9409362	28-04-94	AU-A-	5151493	09-05-94
		CA-A-	2146985	28-04-94
		EP-A-	0671003	13-09-95
		FI-A-	951720	11-04-95
		JP-T-	8502360	12-03-96
		NO-A-	951416	11-04-95
		NZ-A-	256694	27-02-96
		ZA-A-	9307593	03-05-94

WO-A-9408226	14-04-94	AU-A-	5149393	26-04-94
		EP-A-	0663998	26-07-95
		FI-A-	951570	03-04-95
		JP-T-	8501878	27-02-96
		NO-A-	951284	03-04-95
		NZ-A-	256675	27-11-95
		ZA-A-	9307297	25-04-94
		AU-A-	5971994	15-08-94
		BR-A-	9405871	12-12-95
		CA-A-	2154786	04-08-94
		CN-A-	1116878	14-02-96
		WO-A-	9417391	04-08-94
		EP-A-	0681693	15-11-95
		FI-A-	953579	26-07-95
		JP-T-	8505944	25-06-96
		NO-A-	952957	26-07-95
		ZA-A-	9400536	09-09-94

EP-A-0304232	22-02-89	FR-A-	2619623	24-02-89
		FR-A-	2619572	24-02-89
		FR-A-	2619625	24-02-89
		FR-A-	2619626	24-02-89
		FR-A-	2619627	24-02-89
		FR-A-	2619628	24-02-89
		FR-A-	2619629	24-02-89
		FR-A-	2619630	24-02-89
		FR-A-	2634283	19-01-90
		AT-T-	146880	15-01-97
		AU-B-	603919	29-11-90
		AU-A-	2095388	23-02-89
		CA-A-	1333447	13-12-94

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/04599

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0304232		JP-A- 1113637	02-05-89
		US-A- 5452232	19-09-95

EP-A-0285251	05-10-88	FR-A- 2611911	09-09-88
		AU-B- 603868	29-11-90
		AU-A- 1200988	01-09-88
		CA-A- 1321895	07-09-93
		DE-D- 3864432	02-10-91
		JP-A- 63243736	11-10-88
		NO-B- 178448	18-12-95
		US-A- 5490085	06-02-96
